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# A review on phase change cold storage in air-conditioning system: Materials and applications

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ABSTRACT

This paper reviews the previous work on phase change cold storage for air-conditioning systems focusing on two aspects including phase change materials (PCMs) and applications. Besides the studies on phase change cold storage devices, the typical air-conditioning systems with cold storage are also reviewed, namely the solar air-conditioning system with cold storage, latent cooling storage and transport system and mixed cold storage air-conditioning system. Moreover, the problems with respect to compatibility, heat transfer enhancement, phase change properties of composite PCMs, etc., are discussed for further investigation.



**Contents**



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## 1. Introduction

Cold storage plays an important role in conserving available energy, improving energy utilization efficiency and successful load shifting. The electrical energy consumption varies significantly during the day and night, especially in extremely cold climate areas where the major part of the variation is due to domestic space cooling. Therefore, cold storage air-conditioning, as an advocated energy-saving technology, offers a mean to alleviate the peak load on electricity grids and utilize power in the off peak period.

Ice storage is a frequently used cold storage method. However, the evaporating temperature of an ice storage air-conditioning system is lower than that of a conventional air-conditioning system by 8–10 °C, resulting in a decrease in the operating efficiency by 30%–40% [1]. Beside the ice storage, phase change cold storage method has been applied and gained popularity for many years. It employs phase change materials (PCMs) as the cold storage medium, and charges/discharges cooling capacity by the latent heat generated during the phase transition. Main advantages of the phase change cold storage can be summarized as: (1) the storage density of PCMs is 5–14 times higher than that of sensible heat storage materials [2]; (2) the phase change temperature can be adjusted according to the character of the air-conditioning system; (3) the refrigeration unit can operate under a single working condition instead of being integrated with a secondary refrigeration unit; (4) the system efficiency can be largely improved since a higher evaporating temperature is achieved; (5) the temperature swing of a phase change cold storage is much smaller compared with a sensible heat storage. However, there are always some practical difficulties in applying the phase change cold storage method owing to the properties of low thermal conductivity, density changes, poor stability under extended cycling, phase segregation and supercooling of the phase change materials [3].

Among diverse space cooling applications in buildings, this paper mainly focuses on water-cooled air-conditioning systems. The aim of this paper is to summarize some suitable PCMs for cold storage application and enhancements of the phase change behavior and heat transfer properties. Also, a review of optimization methods, including optimized structures of cold storage devices and air-conditioning systems that use a phase change cold storage to improve the energy utilization, is provided.

## 2. Phase change materials

Generally, PCMs for cold storage air-conditioning should have properties as follows: (1) phase change temperature corresponding to the practical range of the evaporating temperature; (2) large latent heat; (3) high thermal conductivity; (4) high freezing and melting rate; (5) large density; (6) small volumetric change between solid and liquid phase (7) freezing and melting congruently with minimum supercooling and without phase segregation, 8) stability in long term phase change behavior; (9) chemically stable, non-toxic and non-corrosive; and (10) low in cost. Based on this, optimization techniques for ideal phase change temperature, latent heat and thermal conductivity of PCMs have been widely studied. Current studies mainly concern tow aspects. For one thing, two or more kinds of PCMs are composited to achieve a required phase change temperature. For another, nanotechnology, microencapsulation and solvent absorption by solid are utilized to achieve appropriate thermophysical properties, especially better heat transfer efficiency.

### 2.1. Composite PCMs

The phase change temperature should correspond with the evaporating temperature of the air-conditioning system so that the working condition of the refrigeration unit and the cold storage unit can be concordant. Several classes of PCM are chosen and composited into binary or multiple mixtures for the purpose of obtaining a designed phase change temperature. According to the phase change temperature in concert with a certain functional air-conditioning system, the composite PCMs can be categorized as follows.

#### 2.1.1. Composite PCMs for low temperature cooling systems

Cold air distribution is a familiar cooling supply application in which the supply air has a much lower temperature and smaller volume. Thus, its chilled water temperature is generally lower than that of a conventional air-conditioning system by 1.4–5 °C. Besides, the chilled water in many industrial air-conditioning systems has an even lower temperature. For example, food industries demand the chilled water at 2–4 °C and pharmaceutical industries generally require the solution temperature as low as $-10$ to $-15$ °C. There are many composite PCMs developed for low temperature cooling application in recent literatures, as listed in Table 1.

#### 2.1.2. Composite PCMs for conventional air-conditioning systems

The chilled water temperature of a conventional air-conditioning system is usually about 7 °C, thus the PCM for cold storage should have a phase change temperature in the range of 5–10 °C. Some suitable composite PCMs are listed in Table 2.

It is reported that the COP of a refrigeration unit increases linearly with the increase of its evaporating temperature [14]. Thus, compared with conventional air-conditioning systems, the evaporating temperature of high temperature cooling systems, such as solar cooling systems and temperature and humidity independent control systems, is always higher in order to achieve a higher COP. Composite PCMs for cold storage of high temperature cooling application with a phase change temperature of 10–15 °C are listed in Table 3.

### 2.2. PCMs with special structures

#### 2.2.1. Nano-composite PCMs

In order to improve the heat conduction, nano-scaled metal or metal oxide particles are added into the base fluid of PCM at

**Table 1**
Composite PCMs for low temperature cooling systems.

| Ingredient | Type | Phase change temperature (°C) | Latent heat (kJ/kg) | Phase transition behavior | | Reference |
|---|---|---|---|---|---|---|
| | | | | Phase change band (°C) | Degree of supercooling (°C) | |
| Dodecanol–Caprylic acid (40.6:59.4 by quality) | Organic | 7 | 178.6 | / | 2.5 | [4] |
| Hexadecane–Tetradecane (2:3–0:1 by volume) | Organic | 1.7–5.3 | 148.1 –211.5 | ≤ 3.2 | 1–2 | [5,6] |
| Caprylic acid–Lauric acid (9:1 by mole) | Organic | 3.77 | 151.5 | 8.23 | / | [7] |

**Table 2**
Composite PCMs for conventional air-conditioning systems.

| Ingredient | Type | Phase change temperature (°C) | Latent heat (kJ/kg) | Phase transition behavior | | Reference |
|---|---|---|---|---|---|---|
| | | | | Phase change band (°C) | Degree of supercooling (°C) | |
| Caprylic acid–Palmitic acid (9:1 by quality) | Organic | 6.54 | 116.5 | $>4.8$ | 2.2 | [8] |
| 40% Tetra-n-butylammonium Bromide adding 2% borax | Inorganic | 9 | 187.0 | 2.0 | 4–6 | [9] |
| 76% $Na_2SO_4 \cdot H_2O$ | Inorganic | 9.3 | 114.4 | 1.05 | / | [10] |
| Hexadecane–Tetradecane (2:1–2:3 by volume) | Organic | 5.3–10 | 147.7 –148.1 | $\leq 3.2$ | 1–2 | [5,6] |
| C14, C15, C16, C17, C18 (33.4:47.3:16.3:2.6: 0.4 by quality) | Organic | 7 | 158.3 | 2 | / | [11] |
| Lauryl alcohol–Caprylic acid (2:3 by quality) | Organic | 6.2 | 173.2 | / | / | [12] |
| HS-1, HS-4, HS-8, HS-9 | Organic | 6.48–8.14 | 143.2 –147.0 | / | 0.42–0.665 | [13] |

**Table 3**
Composite PCMs for high temperature cooling systems.

| Ingredient | Type | Phase change temperature (°C) | Latent heat (kJ/kg) | Phase transition behavior | | Reference |
|---|---|---|---|---|---|---|
| | | | | Phase change band (°C) | Degree of supercooling (°C) | |
| 45% Tetra-n-butylammonium Bromide | Inorganic | 12.5 | 195.5 | / | / | [15] |
| Capric acid–Lauric acid (65:35 by mole) with 10% Methyl salicylate | Organic | 12.5 | 126.7 | 13.7 | / | [16] |
| Capric acid–Lauric acid (65:35 by mole) with 10% Cineole | Organic | 12.3 | 111.6 | 14.0 | / | [16] |
| Capric acid–Lauric acid (65:35 by mole) with 10% Eugenol | Organic | 13.9 | 117.8 | 15.2 | / | [16] |
| Capric acid–Lauric acid (65:35 by mole) with n-Pentadecane (9:1/7:3/5:5 by volume) | Organic | 13.3/11.3/ 10.2 | 142.2/ 149.2/ 157.8 | 12.4/14.4/ 11.1 | / | [17] |
| Hexadecane–Tetradecane (6.5:1–2:1 by volume) | Organic | 10–14.5 | 147.7 –182.7 | $\leq 3.2$ | 1–2 | [5,6] |

certain proportions, thus forming the nano-composite PCM. Nanoparticles can change the structure of the base fluid. They can also change the micro-convection between the base fluid and solid particles as well as between the particles themselves. Thereby, the thermal conductivity of the PCM can be increased.

Kalaiselvam et al. [18] investigated the heat transfer characteristics and thermodynamic behaviors of a PCM with dispersion of alumina and aluminum nanoparticles. The transient temperature variations, moving interface positions, solidification and melting rates were analyzed for six different PCMs in pure form and with dispersed nanoparticles. The six PCMs were 60% n-tetradecane: 40% n-hexadecane, capric/lauric acid, $CaCl_2.6H_2O$, n-octadecane, n-hexadecane and n-eicosane. The results showed that, the solidification time for 60% n-tetradecane:40% n-hexadecane embedded with nanoparticles was expected to reduce by 12.97% and 4.97%, respectively, than at its pure form. It was also noted that the selection of nanoparticles for specific PCMs was an important criterion in determining the charging and discharging rate. The density of the employed nanoparticles had been in the same range as that of the PCM; hence the adverse effects related to the convection losses were prevented.

Li et al. [19,20] employed nano-scaled $TiO_2$ and Cu into an organic PCM. Liu [21] prepared a $TiO_2$–$BaCl_2$–$H_2O$ phase change nano-composite at different volume fractions of $TiO_2$. It was shown that the thermal conductivity of the PCM increased by 19.8% and 26.8% after adding $TiO_2$ and Cu, respectively. The effect of nanoparticles on the thermal conductivity was more notable with the increase of the volume fraction of nanoparticles. Meanwhile, nanoparticles enhanced the charging and discharging rate and lowered the supercooling degree. When the volume fraction of $BaCl_2$ reached 1.13 vol%, the supercooling phenomenon ultimately vanished. It was suggested that the nanoparticles have functions of enhancing heat transfer as well as accelerating nucleation. Li et al. [22] carried out experiments on Cu–$H_2O$ nano-fluid. It was found that, with the increase of the Reynolds number and the mass fraction of Cu particles, the convective heat transfer coefficient increased. The thermal conductivity and viscosity of the nano-fluid and the migration of the particles were main factors to affect the convective heat transfer coefficient.

In order to create a stable, long-lasting and low-reunion nanofluid, practical technologies to disperse nanoparticles into a medium are paid attention to. Liu et al. [21,23] found that the suspension stability of PCMs was mainly affected by the dispersants and pH value of the fluid. Single dispersants such as $Na_5P_3O_{10}$ and $(HOCH_2CH_2)_3N$ and compound dispersants were tested at different dispersive parameters. The compound dispersants showed better effects than the single one. The $TiO_2$–$BaCl_2$–$H_2O$ nano-composite showed the best dispersion characteristics when compound dispersants were added with a pH value of 10. However, it was notable that the presence of nano-$TiO_2$ increased the viscosity of the fluid, and the rise of viscosity intensified as the concentration of the nano-$TiO_2$ went up.

### 2.2.2. Microencapsulated PCMs

Another practical way to enhance heat conduction is to coat the PCM with hydrophilic polymer compound capsules. The capsules are dispersed uniformly in a medium fluid, thus forming a suspension which is the so-called microencapsulated PCM. Microencapsulated PCMs have advantages of increasing heat transfer areas, reducing reactivity of the PCM towards the outside environment, and controlling volumetric change between the liquid and solid phase of the PCM [3]. Methods to form a microencapsulated PCM are: in situ polymerization, interfacial polymerization, suspension polymerization, complex polymerization, sprays polymerization, etc. Generally, materials that can be used as the capsule wall are melamine resin [24,25], urea resin [26], phenolic resin [27], carbamide resin [28], polystyrene [29], gelatin and acacia gum [30], polyacrylate [31], polyvinyl alcohol [32], silica glass [33], epoxy resin [34] and protein [35].

By the use of ultrasound technology and mini-emulsion in situ polymerization, Fang et al. [36,37] developed a microencapsulated PCM with polystyrene as the capsule wall and octadecane as the capsule core. The mean diameter of the microcapsule was

124 nm and the phase transition enthalpy was up to 124.4 kJ/kg. Xing et al. [38] used donkey-hide gelatin and arabic gum together as the wall while tetradecane as the core to develop a microcapsule of 1–20 μm. By Differential Scanning Calorimeter (DSC) and Thermal Analyzer, the melting and freezing point of the PCM were tested at 5.792 °C and 2.564 °C with the latent heat of 191.9 kJ/kg and 189.2 kJ/kg, respectively. Taguchi et al. [39] employed methyl methacrylate as the wall and pentadecane as the core to create a microcapsule which has a phase change temperature of 9.5–10 °C and latent heat of 97–107 kJ/kg. In the experiment, methyl methacrylate, acting as the PCM, was adsorbed in lipophilic polymer particles. The volume of the PCM monomer and the soaking time for the oil absorbable polymer particles to soak into the PCM were changed stepwise. The phase change temperature and latent heat decreased with the increase of the adsorbed volume of PCM. Furthermore, the leakage of PCM from the microcapsules was no longer observed when the volume of PCM reached 5 $cm^3$ and 10 $cm^3$.

A successful way to enhance the thermal capacity of chilled water systems is to employ microencapsulated PCM slurries. The heat transfer characteristics, fluidness and stability have been widely investigated in order to assess its applicability for the integration into a cold storage system. Bogdan et al. [40] developed a new PCM slurry based on microencapsulated Rubitherm RT6 at high concentration (45 wt%). It was found that the heat transfer coefficient of the PCM slurry went up to 5 times that of water depending on temperature conditions. No significant change was observed between the results of two DSC measurements carried out at an interval of approximately two weeks. Huang et al. [41] studied a paraffin/water emulsion for cooling systems. The emulsion was a binary fluid comprising a collection of small Rubitherm RT10 paraffin droplets with a melting temperature range of 2–12 °C and a dimension of 1–10 μm, which was dispersed in water by a nonionic surfactant. The heat capacity and rheological behavior of the samples containing 15–75 wt% RT10 were studied. The results indicated that the emulsion containing 30–50 wt% paraffin was suitable for practical applications because it had an energy density which was two times that of pure water and a relatively low viscosity. An emulsion containing 35 wt% RT10 was circulated in a test rig for six days. No distinct change in properties was observed after 50 freezing and melting cycles. PCM mass concentration is a crucial influencing factor that affects the properties of PCM slurry, especially the convection heat transfer efficiency. Inaba et al. [42] conducted experiments in rectangular enclosures in dealing with the natural convection heat transfer characteristics of a microemulsion composed of fine PCM particles, water and surfactant. The PCM mass concentration of the slurry varied from a maximum 30 wt% to a diluted minimum 5 wt%. The results showed that the Nusselt number increased slightly with the increase of the PCM mass concentration in solid phase. In the phase change temperature range, the Nusselt number increased with the rise of the PCM mass concentration at low Rayleigh numbers, while it decreased with the drop of the PCM mass concentration at high Rayleigh numbers. There was no big difference in the natural convection heat transfer of the slurry with low PCM mass concentrations ($<10$ wt%). However, the difference became obvious as the concentration increases.

PCM slurry can be applied in a wide range of cooling systems. Generally, they can be classified into a dynamic type and a static type. In a dynamic type, the PCM slurry is transported to heat exchangers or air-conditioning terminals directly. The system has functions of slurry producing, storing and transporting, and is usually defined as latent cooling storage and transport system. As for a static type, the quiescent PCM slurry is stored in a thermal tank. Wang et al. [43] proposed a novel design of cooling ceiling operating together with a PCM slurry thermal storage. The ceiling panels removed sensible load by the circulation of slurries. The dehumidified air treated by an air handing unit removed latent load and part of sensible load. The annual energy consumption of three systems, namely cooling ceiling with PCM slurry storage, cooling ceiling with ice storage and cooling ceiling without thermal storage, were compared based on an office room. It was concluded that the combined system of cooling ceiling with PCM slurry storage presented the highest energy efficiency. At high electricity tariff ratios, the complete load shifting of the cooling load from daytime to nighttime by the PCM slurry storage was feasible and economical.

### 2.2.3. Shape-stabilized PCMs

Another PCM encapsulating technology has been developed in order to overcome the fluidity defect of solid–liquid PCM. PCMs are put into solid porous matrixes, such as polyethylene, polymethacrylic acid and polystyrene resin, etc. It can be obtained by melting, physical blending method or chemical reaction method. For example, Li et al. [44] prepared a composite by paraffin and high-density polyethylene (HDPE). The paraffin and HDPE were blend and melted. When temperature dropped, the HDPE froze first, while the paraffin was still in liquid phase and bounded in the space network of HDPE. Thus the shape-stabilized paraffin/HDPE was formed. Shape-stabilized PCMs have salient features. They have large specific heat in phase change temperature region as well as suitable thermal conductivity. Also, they can maintain a certain solid form during phase transition without need for containers.

Shape-stabilized PCMs are usually embedded into floor and wall board of buildings for space cooling. They are considered prospective in buildings at certain climatic zones with a good potential for reducing cooling loads by enhancing the storage capacity of the building envelope [45]. Ma et al. [46] used a capric acid and lauric acid eutectic mixture as the base fluid and porous graphite as the matrix to develop the capric–lauric acid/expanded graphite PCM. The base fluid was totally encapsulated in the graphite holes with the mass fraction of 80.47%. Using DSC and Environment Scanning Electron Microscope, the thermal conductivity of the shape-stabilized PCM was found to be much higher than that of a single base fluid. The melting and freezing time were reduced by 74.1% and 84.9%, respectively. Sari et al. [47] absorbed capric acid into expanded perlite with the adsorption ratio up to 55%. When 10% expanded graphite was absorbed, the thermal conductivity increased by 64%. Moreover, the shape-stabilized PCM showed a good thermal stability without leakage even after 5000 melting and freezing cycles. Zhang et al. [48] embedded a composite paraffin material into a polymer board. The phase change temperature could be adjusted by changing the paraffin type. To improve the thermal conductivity, researchers added some additives into shape-stabilized PCMs. Zhang et al. [49] found that most efficient conducting additive was ex-foliated graphite. The thermal conductivity evolved from 0.150 W/m K to 0.229 W/m K after adding 10 wt% graphite.

A novel application of shape-stabilized PCM was studied. Lafdi et al. [50] employed foam structures impregnated with PCMs as heat sinks for cooling of electronic devices. Different design parameters were simulated and compared such as the foam properties (porosity, pore size, and thermal conductivity), heat sink shape, orientation, and use of internal fins inside the foam composite PCM. It was shown that, for steady heat generation, the shape and orientation of the composite heat sink had significant impact on the system performance. Using PCMs in heat sinks was an effective solution especially when the system experienced various levels of energy spikes, due to the heat absorption inside

the PCM as latent heat during the energy spike period and the heat release during the minimum heat generation period.

## 3. Phase change cold storage device

There are several options for the PCMs to be used to meet the cooling requirements. They can be integrated into building's envelope to increase thermal storage density of buildings [51–61]. It is also possible to install PCMs into air-conditioning systems as cold storage devices. The former is mainly based on a passive or active air flow to exchange heat and provide cooling, while the latter operates in the manner of the circulation of heat transfer fluid (HTF), which is usually water. Due to the notable advantage in the specific heat of water compared with air, the latter plays a significant part in space cooling application. In such cold storage air-conditioning systems, the PCM is filled into a cold storage device which is placed in the chilled water side of the system, as shown in Fig. 1. During off peak periods, the chiller produces and provides cooling to the cold storage device by water (cycle 1). When the cooling load gets higher and more cooling is needed, the stored cooling energy is released from the storage and is supplied to user through air-conditioning terminals (cycle 2). When the stored cooling is not enough to meet the requirement, the chiller starts to provide cooling directly to the user (cycle 3). There are diverse structures of cold storage device, namely spherical capsules packed bed, flat-plate, double tube, shell and tube with internal flow, shell and tube with parallel flow and shell and tube with cross flow [62].

### 3.1. Spherical capsules cold storage

Spherical capsules cold storage, which is frequently used, is to encapsulate PCMs into polyethylene balls and accumulate the balls in a cold water tank. The water exchanges heat directly with the balls, and the PCM freezes and melts from outer sphere to inner sphere.

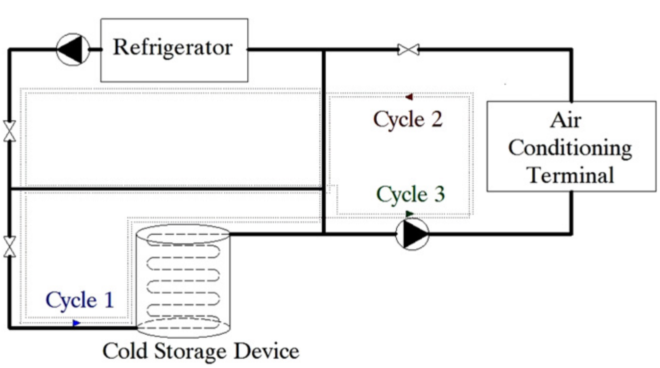


**Fig. 1.** Diagram of phase change cold storage air-conditioning system.

#### 3.1.1. Theoretical analysis

The basic component of this cold storage is the spherical capsule. The schematic picture in Fig. 2 shows the phase interface movement of spherical capsules. During the freezing process, the phase interface movement is relatively fast at the initial stage since thermal resistance is small. The thermal resistance increases and lowers the freezing rate as the solid fraction of PCM increases. As the liquid fraction of PCM shrinks, energy needed for phase transition reduces, thus the freezing rate rebounds slightly at the final stage [63]. During the melting process, the heat transfer is mainly based on heat conduction in the initial stage. Convection is enhanced as the phase transition proceeds [64]. In actual conditions, unfixed melting occurs, which is resulted from the float of the solid PCM caused by the solid–liquid density difference. It is deduced that the unfixed melting intensifies heat transfer and speeds up the melting process. Additionally, unfixed melting is much closer to the actual melting behavior, thus a more accurate value of discharged cooling and melting rate can be obtained based upon the theoretical analysis of unfixed melting [65].

The factors that affect the storage capacity, storage rate and other performance parameters of the spherical capsule are theoretically studied. It is shown that the phase change time can be shortened by the following means: uniformize the solid–liquid mixture [66], decrease the diameter of spherical capsule [63–65,67–69], shape the spherical capsule more ellipsoidal [70], make the initial temperature of the PCM closer to its phase change temperature [69], decrease the temperature of HTF [63,65,68–70], increase Ste number [64] and keep the HTF flow direction inverse the gravity [71]. Concerning the optimization of the spherical capsule, there are still some problems. Jin Jing et al. [66] found that the nucleation freezing could increase the storage rate compared with the annulus freezing. However, there seems no practical instruction given to motive nucleation and form a uniform solid–liquid mixture. As for the diameter of the spherical capsule, it is indicated that the freezing time shrinks significantly with the decrease of diameter. Zhang et al. [69] found that the freezing time of a spherical capsule with the diameter of 100 mm was 2.4 times that of a capsule with the diameter of 50 mm. However, as the capsules with smaller diameter are accumulated in the tank, the flow resistance will rise greatly. From this viewpoint, capsules should better be fabricated to be small within a certain limit. However, the capsules with larger diameter might be rational on the condition that the storage time is acceptable. Also, the heat transfer temperature difference, storage rate and thermal properties of the PCM should be taken into account when choosing a proper capsule diameter [68].

Mathematical modeling is also used to predict the operation of a cold storage device. Charging and discharging capacity and outlet temperature of HTF are important parameters to evaluate the performance of a cold storage tank. Li et al. [13,72] divided a storage tank into M control bodies along the height. Each control body contained 1/M total amount of the spherical capsules, as shown in Fig. 3. Wu et al. [73] studied a spherical capsules packed bed using n-tetradecane as the PCM and aqueous ethylene glycol solution with 40% volumetric concentration as the HTF. The influencing factors were concluded as: (1) the PCM at outlet

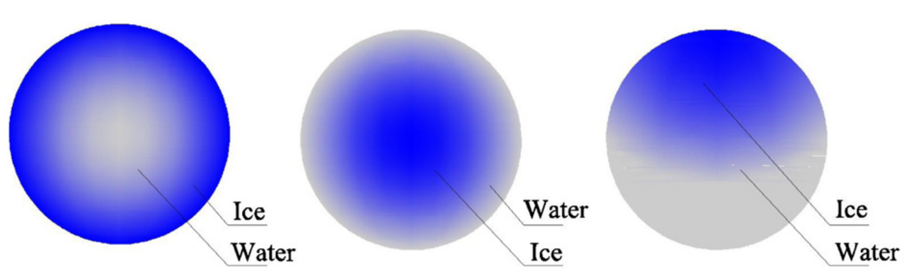


**Fig. 2.** Schematic picture of a spherical capsule (from left: freezing, fixed melting, unfixed melting).

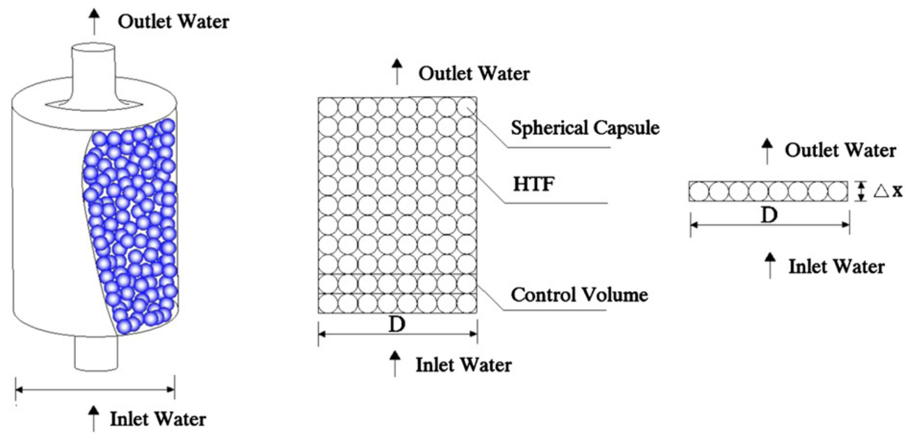


**Fig. 3.** Model of spherical capsule cold storage tank [72].

position took more time to complete solidification and melting; (2) the time for complete solidification and melting decreased as the flow rate of HTF increased. Higher flow rate of HTF also resulted in higher storage and releasing rate; (3) the inlet HTF temperature had strong effects on the performance of both charging and discharging process. The time for complete solidification increased as inlet HTF temperature increased, whereas the complete melting time decreased with increasing inlet HTF temperature; (4) lower porosity of the packed bed indicated higher storage capacity, and hence longer time was required for complete solidification and melting. Additionally, the effect of flow direction of HTF was studied by Kousksou et al. [74] by establishing a two-dimensional porous medium model of a cylindrical cold storage tank. It was concluded that due to the directional consistency of the natural convection and the forced convection in vertical direction, the vertical flow of HTF led to better charging performance. Moreover, structural optimization methods were put forward, such as filling copper foam or aluminum foam into the storage tank. It was found that the foam metal filler could greatly enhance heat transfer of the tank in all directions, and made the inner temperature more uniform [75]. Different capsule materials were compared by Ismail et al. [76]. They built a transient one-dimensional model and divided the tank into a number of axial layers, of which the thickness was always equal or larger than the capsule diameter. The complete charging time was found to be 7 h for the case of copper, 8 h for the case of polyethylene and 9 h and 20 min for the case of polrvinyl chloride (PVC). The variation in charging time was relatively small, and hence the use of polyethylene or PVC for capsule facilitated the construction of the storage and reduced its costs.

#### 3.1.2. Experimental investigation

The experiments on spherical capsules are conducted employing a homothermal water circulator [69], while the experiments on cold storage devices are usually done in an integrated system. Some of them are to verify the theoretical results, while others are to evaluate the system performance such as the cooling capacity, stability and thermal comfort. Liu and Li et al. [63,64] made an experimental verification on the difference between fixed melting and unfixed melting by establishing a small cold storage system. Wu et al. [77] measured the supply air temperature of a cold storage air-conditioning system. The supply air temperature was stable at 16 °C and the indoor air temperature was about 22–23 °C, which could meet the thermal comfort standard. Fan [78] prepared a PCM with the phase change temperature of 2.64 °C and applied it in a low temperature refrigerator. The temperature of the refrigerator used to wave within a range of 2 °C. However, it became smooth without obvious fluctuation after adding the PCM. Bédécarrats et al. [79] investigated a test plant which was a tank filled with randomly dispersed spherical capsules. In the charge mode, supercooling was observed when the inlet HTF temperature maintained lower than the freezing temperature. It assigned a stabilization of the outlet HTF temperature at a value higher than the inlet HTF temperature but lower than the melting temperature. In the discharge mode, when the inlet HTF maintained at a temperature higher than the melting temperature, a quasi-stabilization of the outlet HTF temperature was observed to be a function of the values of inlet temperature and flow rate of HTF. The charging and discharging time both decreased as the flow rate HTF rose. Also, the charging time decreased as the inlet HTF temperature got lower and the charging time decreased as it got higher.

### 3.2. Shell and tube cold storage

Shell and tube cold storage is another popular type. It is usually fabricated as a cylinder or rectangular container, which consists of horizontal or vertical parallel curved pipes submerged in the quiescent PCM with the HTF flowing through the pipes. There are also conditions that the quiescent PCM is contained in parallel pipes and the HTF flows across the pipes externally. In both cases, phase transition happens along the external or internal wall of the pipe. The influencing factors on the performance mainly concerns the heat transfer properties, namely the inlet HTF temperature, Prandtl number, Reynolds number, length and radius of the tube, etc.

Anica et al. [80,81] studied a shell and tube cold storage system. The experimental and numerical investigations of the solid–liquid phase change of the PCM, the transient forced convective heat transfer between the tube wall and the HTF with moderate Prandtl numbers, and the heat conduction through the wall were presented based on the enthalpy formulation. The unsteady temperature distributions of HTF, PCM and tube wall were obtained by a series of numerical calculations for various HTF working conditions and various geometric parameters. The results showed that the HTF velocity field reached the fully developed condition quickly, while the temperature field had never reached a steady state condition due to the moving melting and solidification fronts. Owing to the relatively large Prandtl number of the water, the heat transfer from the HTF to the PCM was slow. Therefore, a large amount of heat was carried downstream with the HTF, while a small amount of heat was

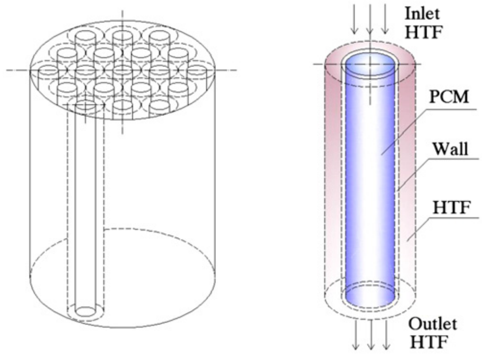


**Fig. 4.** Model of shell and tube cold storage tank [82].

transferred directly to the PCM upstream. Also, the selection of the operating conditions and geometric parameters dimensions depended on the required heat transfer rate and the charging/discharging time. Wu et al. [82] studied dynamic discharging characteristics of a coil pipe cold storage, as shown in Fig. 4. N-tetradecane was taken as the PCM and aqueous ethylene glycol solution with 25% volumetric concentration was used as HTF. During discharging process, the temperatures rose quickly to 7.79 °C in the sensible heat phase of the solid PCM, maintained during the latent heat phase and approached gradually to 15 °C in the sensible heat phase of the liquid PCM. The discharging rate decreased quickly to 5.4 kW in the initial period, before it decreased almost to zero when discharge completed. It was indicated that higher flow rate and higher inlet HTF temperature resulted in higher discharging rate, whereas the diameter of coil pipe had little influence on the discharging characteristics.

Heat transfer characteristic is a crucial parameter of cold storage devices as it has the direct bearing on the operating performance. Each type of cold storage has its particular heat transfer characteristics, thus the optimization methods seem to be diverse. Spherical capsules only touch on the radial thermal conduction. However, the axial temperature distribution should also be taken into account when the capsules are positioned in a cylindrical tank. The inner structure of the tank, namely the layers along the axial and the number of capsules in each layer, matters a lot. Cylindrical PCM tank undergoes varying convection heat transfer temperature difference along the axial as well as varying thermal conduction temperature difference along the radial. Therefore, the diameter and space interval of adjacent PCM containers and the height of the tank largely affect the cold storage performance. Liu et al. [83] analyzed a cold storage unit containing encapsulated PCM flat slabs. An aglycol based HTF and a PCM with the melting temperature of 26.7 °C and were utilized. The main conclusions were: (1) The higher the HTF flow rate the quicker the PCM melting process; (2) the increase of the difference between the inlet HTF temperature and the PCM melting temperature led to an exponential decrease in the melting time; (3) the reduction of the gap between adjacent PCM slabs slightly increased the heat transfer rate during melting process. However, the heat transfer rate during initial sensible period was significantly enhanced by reducing the gap; (4) The effects of the ratio of length to width and the thickness of the slab were limited; (5) the PCM initial temperature only affected the initial melting process before reaching the melting point.

To sum up, the influencing factors on the heat transfer performance of different types of cold storage can be considered to be similar. As to the HTF, higher flow rate, more turbulent flow pattern and larger temperature difference between the HTF and the PCM contribute to higher charging and discharging rate. As to the PCM, the thermal conductivity, initial temperature and phase change characteristic (heat of fusion, nucleation rate, supercooling degree, etc) should be taken into account. As to the PCM container, the size, ratio of length to width (or height to diameter), porosity, thickness and material of the wall are important structural factors. However, the effects of structural factors seem to be limited compared with the other two aspects. Moreover, the internal thermal conductivity of PCM containers can also be enhanced through structures such as metallic fillers, fins, aluminum shavings, metal honeycombs, metal matrices, rings, metal fibers or graphite, high conductivity particles, etc [62].

## 4. Typical air-conditioning systems with phase change cold storage

### 4.1. Cold storage solar air-conditioning system

Solar energy systems in combination with thermal driven sorption chillers for air-conditioning are gaining increasing attention. For solar cooling, a backup system is necessary for times when no sufficient solar energy is available [84]. Solar energy is available only during daytime, and hence, its application usually requires an efficient thermal energy storage so that the excess cooling produced during sunshine hours may be stored for later use during the night [3]. Moreover, solar cooling systems are usually intermittent and susceptible to the weather. Therefore, applying cold storage methods to solar cooling air-conditioning systems is favorable to utilize renewable energy and enhance system stability. General structure of a solar cold storage air-conditioning system is shown in Fig. 5. The charging/discharging process is similar to that of a general cold storage air-conditioning system. When sunshine is sufficient, the chiller transforms solar energy into cooling capacity, and the cooling is stored by means of the phase transition of the PCM. When sunshine is inadequate, the PCM discharges, and the released cooling is supplied to users.

The thermal storage for solar air-conditioning systems can be realized in two different ways, either storing the driving heat collected by solar collectors or storing the cooling produced by chillers [84]. The former is widely paid attention to, however, only a few applications have been reported about the latter, most of which are sensible thermal storage with cold water. A home-scaled solar absorption cooling air-conditioning system was built in Cardiff University [85]. The system consisted of a 12 m$^2$ vacuum tube solar collector, a 4.5 kW LiBr/$H_2O$ absorption chiller and a 1000 L cold storage water tank. When the insolation peak

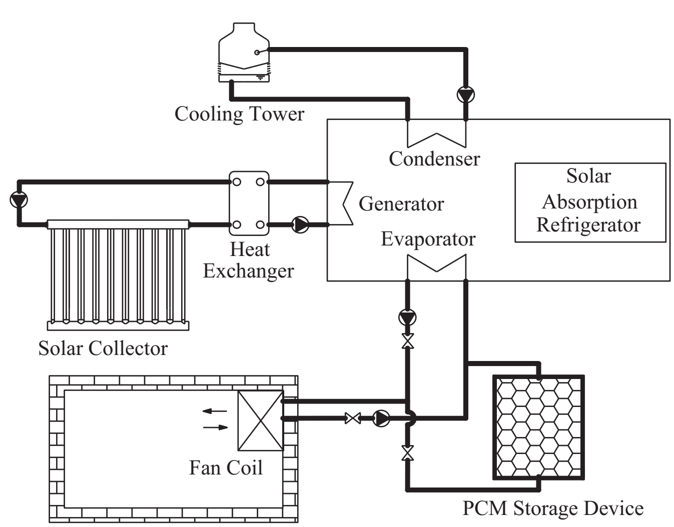


**Fig. 5.** Diagram of a solar air-conditioning system with cold storage.

was 812 W/m$^2$ and average ambient temperature was 24 °C, the chilled water temperature was 7.4 °C and the average system COP was 0.58. However, it required 180–250 l water to store 1 kW cooling energy, which extremely enlarged the size of the storage tank. Such researches were also done by Rosiek et al. [86], Chidambaram et al. [87] and Ortiz et al. [88], etc. There was a common problem in the utilization of water storage reported in these literatures. The volume of the storage tank is usually large since the small storage density of water.

The volume of the tank can be reduced efficiently by applying latent heat storage. It was reported that the cold storage could be better performed by using the latent heat of refrigerant water and strong lithium–bromide solution. Thus, a remarkable higher energy density can be attained and the device can be cheaper due to the small size. Based on this, an experimental setup of an absorption chiller was presented by Lemke et al. [84] which facilitated the supply of a constant cooling load at constantly high COP in spite of periodically available driving heat. Further, it not only improved the performance of cascading chiller but opened up a wider field of applications for thermally driven sorption chiller for solar-assisted cooling. Bogdan et al. [89] carried out a simulation on a solar-assisted ejector cooling system with low temperature PCM cold storage for an office building with cooling requirements during working hours only. Three different circuit configurations and operating principles (with or without a secondary storage) were compared based on the required storage capacity, efficiency and COP. It was found that both the efficiency and COP of the system reached the highest value in case that the configuration had a single storage, followed by the configuration with a secondary storage under the control strategy that the ejector cycle switched on only when the solar irradiation was above inferior limit and the cooling load was above zero. It was also found that the COP of ejector was the parameter with the most significant influence on both efficiency and COP of the system for all the configurations considered.

Absorption cooling systems based on water/lithium bromide solution typically require an open wet cooling tower to transfer the reject heat to the ambient. Yet, water consumption, the need for water make-up and cleaning, formation of fog and risk of Legionella bacteria growth are hindering factors for the implementation of small solar cooling systems. Other from being integrated with the evaporator of air-conditioning system, the latent heat storage can also support the heat rejection of the absorption chiller in conjunction with a dry cooling system thus eliminating the wet cooling tower. The system scheme was presented by Helm et al. [90], as shown in Fig. 6. By this means, heat rejection of the chiller was shifted to periods with lower ambient temperatures (night time or off-peak hours). For the latent heat storage, $CaCl_2 \cdot 6H_2O$ with the phase change temperature in the range of 27–29 °C was applied. Due to the limited temperature swing available for the given application, the storage provided a 10 times higher volumetric storage density in comparison to conventional water storage. The storage capacity of 10 kW and the storage content of 120 kW h were in good agreement with the thermal design and thus proved the feasibility of the storage concept based on heat transfer by a capillary tube register.

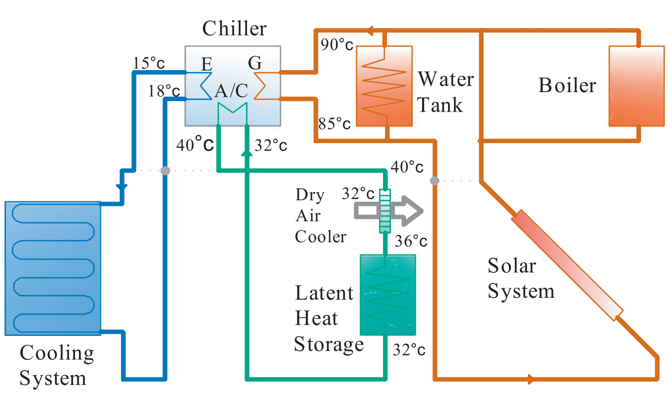


**Fig. 6.** System structure of a solar cooling system with latent heat storage for chiller cooling [90].

### 4.2. Latent cooling storage and transport system

Latent cooling storage and transport systems based on PCM slurries seem to be a promising air-conditioning technology since the slurries have an advantage of small supercooling and high latent heat. Tetra-n-butylammonium bromide (TBAB) is recognized as a rational substitute for water. The slurry of TBAB (CHS) with a good fluidness can be pumped through the pipeline system. When the concentration of the TBAB solution is 40.5%, its phase change temperature is about 12 °C. If NaCl is added with the mass fraction of 6–8%, its phase change temperature reduces to 6–8 °C. The diagram of a latent cooling storage and transport system using CHS is shown in Fig. 7. The system includes a refrigeration link, a CHS generator-storage link, and a delivery link. The cold storage density of the CHS is in the range of −70 to −100 kJ/kg, which is equal to 3.33–4.76 times that of water. Therefore, the circulation flow rate is 1/4–1/3 that of a chilled water system. As a result, the energy consumed to transport cooling only covers 35–50% that of a chilled water system. In addition, due to the high volumetric storage density, the size of CHS storage units can be significantly reduced [91,92]. In addition to TBAB, slurries of other microencapsulated PCMs can also be used in latent cooling transport systems. Fang et al. [36,37] prepared a PCM with polystyrene as the wall and octadecane as the core. Zhang et al. [93] developed a latent functional thermal fluid which had a remarkable fluidness thus could be regarded as a Newtonian fluid. The viscosity was about 5.57 times that of water. Chen et al. [94] used bromo-hexadecane to develop a PCM slurry which had a heat transfer efficiency of 1.42 times that of the water.

Heat transfer behavior and flow characteristics are of the most importance to the utilization of PCM slurries. The heat transfer behavior includes both convection heat transfer between the

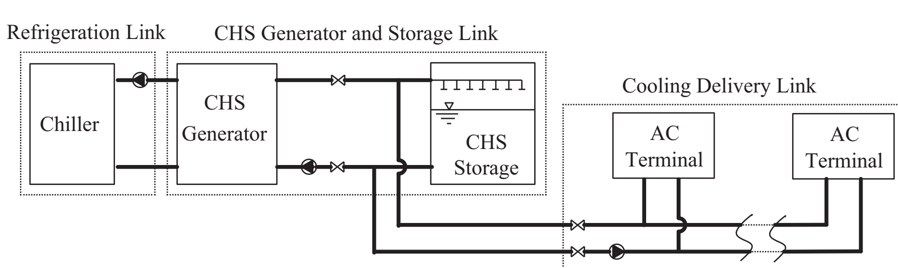


**Fig. 7.** Diagram of a TBAB latent cooling storage and transport system [91].

basic fluid and PCM particles and the heat conduction within the PCM particles. It is affected by the flow turbulence and the PCM particle number. Xiao et al. [95] measured the convection heat transfer coefficient of the CHS in a horizontal tube under constant heat flux boundary condition. It was observed that the perturbation of solid particles and the drop of surface viscosity destroyed or attenuated the CHS momentum boundary layer and, as a result, the heat transfer coefficient could be improved. Nie et al. [96] analyzed the relationship between the TBAB fraction and the thermal conductivity of CHS. The thermal conductivity of CHS decreased within the range of 0.4–0.6 W/m·K when the mass fraction of TBAB increased from 5% to 30%. It was also observed that when the slurry volume fraction varied from 10% to 40%, the thermal conductivity rose from 0.5 W/m K to 0.6 W/m K. El Rhafiki et al. [97] dispersed a composite PCM of hexadecane, octadecane and water into an emulsified medium which contained water, glycerol and surfactant. The freezing process was shortened as the mass fraction of the dispersed PCM reduced. In order to optimize the heat transfer efficiency of slurries, Alvarado et al. [98] did heat transfer experiments on a PCM slurry. It was showed that the use of enhanced tubing could improve heat transfer beyond the current levels. The enhanced surface tubing was more advantageous at a low mass fraction than at a high mass fraction. Particle migration toward the near-wall region before, during and after the bulk fluid reached the melting point was affected by slurry velocity more notably than by heat flux. However, due to the melting and crystallization behavior, the latent heat transition of the slurry running in a practical air-conditioning system seemed not entirely complete. The utilization ratio of the latent heat was related to the desired temperature of the slurry [99].

With respect to the flow and deposition characteristic of PCM slurry, Wang et al. [100] found that when the initial TBAB concentration was less than 20%, CHS formed a uniform hydrate slurry without obvious adhesion. When the initial TBAB concentration was more than 20% and the temperature was 4–5 °C, CHS formed a large number of hydrates. The hydrates tended to adhere on the pipe wall, which was bound to decrease the flow area of the pipe. By adding Span80 with the concentration of over 3%, aggregation of the particles would effectively slow down. Ma et al. [101] studied the energy transport capability of a PCM slurry based on Rubitherm RT6 through a cold storage air handling system for various concentrations and pump powers. It was concluded that the concentration ratio of the slurry largely affected the transport capability and hence the performance of the energy transport system as a whole. The slurry with a concentration at the vicinity of 45% was difficult to be pumped through the cooling coil system. Slurry with a concentration of 25% showed the highest transport capability and the highest system energy transport effectiveness. The transported energy increased with the increase of the pumping rate more obviously at lower concentration than higher concentration (>30%). A decrease in the working temperature range improved the merit of PCM slurry compared with pure water. Alvarado et al. [98] also found that the PCM slurry made by microencapsulating 99% n-tetradecane with gelatin exhibited a Newtonian-like behavior at mass fractions below 17.7% and the relative viscosity was independent of the temperature. Microcapsules became durable and impact-resistant when smaller than 10 μm. The pressure drop experiments revealed a possible drag-reducing effect.

### 4.3. Mixed cold storage air-conditioning system

A mixed cold storage air-condition system is a combination of a PCM cold storage tank, an ice cold storage tank, a refrigeration unit and a cooling supply unit, as shown in Fig. 8. The operation mode is as follows. (1) When the return water temperature of the ice tank reduces to 8 °C, the PCM tank begins to store cooling energy and the PCM start to freeze; meanwhile, the ice tank provides cooling to the user. When the return water temperature of the ice tank rises to 14 °C, the PCM tank stops storing cooling and the HTF is used to charge the ice tank. (2) As the building cooling load rises, the return water temperature of the ice tank increases. When the return water temperature reaches 14 °C and the ice tank cannot meet the cooling requirement alone, both the ice tank and the PCM tank begin to release and supply cooling to the user. (3) When the building load gets lower, all the cooling is supplied by the ice tank. The experimental studies showed that the PCM cold storage tank could increase COP of the chiller by more than 5% and increase cold storage capacity by 20%. Furthermore, the temperature distribution within the ice tank of the mixed cold storage system was more uniform than that of a single ice cold storage system. Also, the discharging rate was steadier [78,102–104].

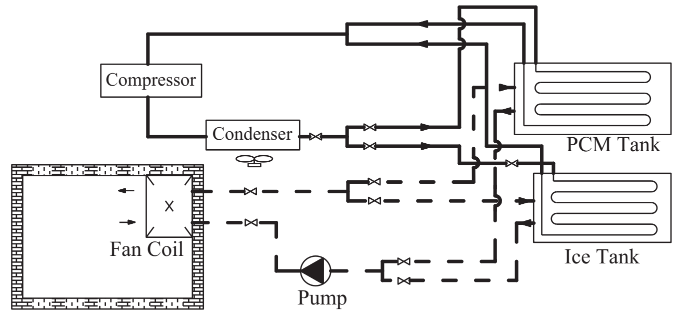


**Fig. 8.** Diagram of a mixed cold storage air-conditioning system [102].

## 5. Conclusions

The phase change cold storage method is capable of improving the efficiency of air-conditioning systems due to the appropriate phase change temperature and high storage density. Recently, studies on PCMs for cold storage in air-conditioning systems mainly concern two aspects – materials and applications, as shown in Fig. 9. As to studies on PCMs, the first step is to composite PCMs to achieve an appropriate phase change temperature. The second is to change the structure of PCMs by adding nanoparticles or by packaging the materials with capsules or porous medium in order to achieve desired thermophysical properties. A common application is to fill the PCMs into cold storage devices, which are usually placed in the chilled water side of air-conditioning systems. Theoretical and experimental studies have been conducted on spherical capsule, shell and tube and other types of cold storage devices. The main items including heat transfer characteristics, temperature distribution and related influencing factors during the solidification and melting process have been investigated. Generally speaking, the performance of the storage can be optimized according to both operational factors and structural parameters. Based upon the existing researches, the technology of PCM storage seems to be practical in solar air-conditioning systems, latent cooling storage and transport systems, mixed cold storage air-conditioning systems and some other novel air-conditioning systems.

However, some problems which still remain a number of topics to be investigated are discussed as follows.

### 5.1. Capability of PCM and container

It is known that non-organic materials, such as salt hydrates, generally have corrosiveness toward some metal and metallic

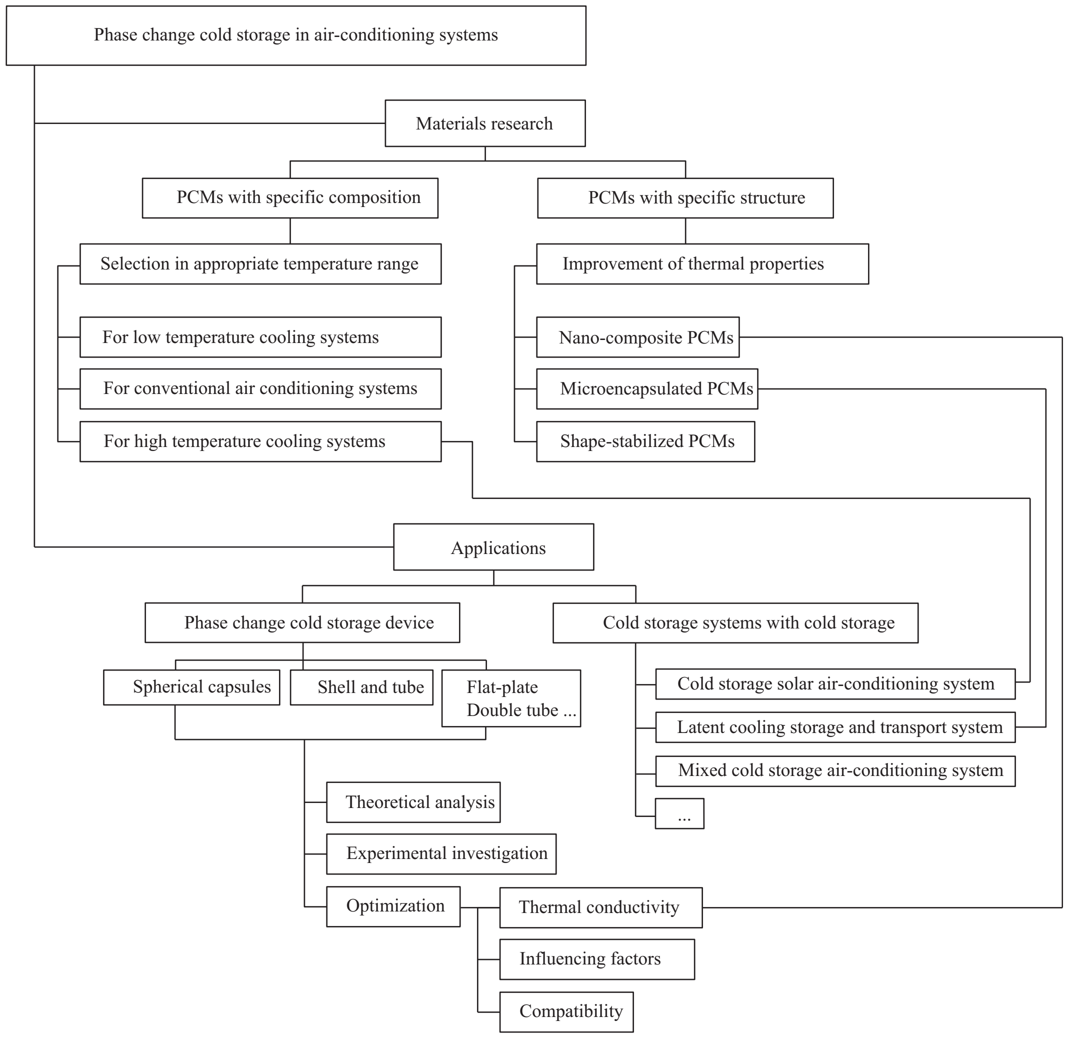


**Fig. 9.** Development and focus on phase change cold storage in air-conditioning systems.

oxide. Also, they may experience high volumetric changes after the phase transition. Nucleating agents are usually needed and often become imperative after repeated cycling [52]. As for organic materials, such as fatty acids and paraffin, may dissolve with some organic capsule materials in consideration of the like dissolves like theory and, even more serious, some are flammable. The repeated heating and cooling processes during practical cold storage systems require higher standard of stability eliminating corrosiveness and dissolubility. However, there are few sufficient experimental determinations with regard to the compatibility of a certain PCM and its container material, and few quantitative criteria have been used to confirm the stability of the cold storage device in long-term operations [105].

### 5.2. Enhancement of heat transfer by convection

Most PCMs employed in commercial thermal storage systems have low thermal diffusivities. Convection is a more effective mechanism for heat transfer than conduction; it is easier to supply energy for the melting process than to withdraw energy during solidification. The variation of surface heat flux depends on the predominance of the convective resistance and the conductive resistance. If the conductive resistance is dominant, the surface heat flux will have a decreasing trend with time. Whereas, when the convective resistance is dominant, nearly uniform surface heat flux can be achieved [62]. However, convection is usually ignored in simulations, which results in the discrepancy between theoretical results and experimental results. Therefore, the convection is suggested to be emphasized in the theoretical analysis and simulation, which makes the calculation of heat transfer rates between the HTF and PCM more accurate. Thus the design of commercial PCM cold storage systems can be more rational.

### 5.3. Enhancement of solidification by dynamic ice-making

Dynamic ice-making technology offers superior efficiency, in which ice is produced on the cooling surface and removed from it, thus eliminating the heat conduction resistance and increasing the COP of the system. In such cases, the heat flux should be maintained under a certain limit so as to remove the ice naturally by either buoyancy forces or liquid flow rather than by mechanical energy. Most dynamic types use water solution as the PCM, however, the depression of freezing point and decrease of latent heat usually occur. Such methods would be promising if they were utilized in PCM cold storage systems. Solid PCMs can be removed from the cooling surface in the same manner. Apart from water, ethylene glyco, propylene glycol and polymer gel are all feasible solutions for crystal manufacture [106–109]. Methods relating to this, such as maintaining the fluidity of the solid–liquid PCM mixture and uniformizing the solidification/melting of the stored liquid/solid PCM layer, are widely proposed [110].

### 5.4. Non-sole phase change temperature of composite PCMs

Different from pure PCMs which have a sole and constant phase change temperature, composite PCMs commonly present a phase change range rather than a phase change point during the phase transition. The temperature range can be observed by DSC or cooling curve testing and is considered to depend on both the heating or cooling rate and the mixture composition [111]. Two aspects may be deserved to be taken note. On one hand, the end of phase transition cannot be estimated visually by the cooling or heating temperature history, while the charged and discharged cooling capacity determined by heat flux measurement would be more accurate to be relied on. On the other hand, since the phase transition happens in a range of temperature, there is a band of solid–liquid mixture rather than a transition interface at a moment. Considering this characteristic, Ismail et al. [112] divided the numerical methods for the solution of phase change problems into two groups: fixed grid methods based on the enthalpy concept, and moving grid methods utilizing the interface immobilization technique. Furzerland [113] compared the two methods for the solution of a specific test problem of one dimension heat transfer by pure convection. One of these conclusions was that the enthalpy method was easier to program and more suitable for PCMs with a range of fusion temperatures.

### 5.5. Performance of low grade energy utilization

Phase change cold storage methods have been used in air-conditioning systems driven by low grade energy, such as solar absorption and adsorption cooling systems. In order to increase the COP of such systems, the chilled water is usually controlled to maintain a temperature higher than that of a system driven by electricity. Besides, the chilled water temperature depends largely on the solar irradiance and other natural conditions, which are available only in certain period of the day. Consequently, more researches are still necessary to enhance the storage efficiency under such poor and unstable working conditions. To cohere with the relatively high temperature chilled water produced by low grade energy driven systems, radiant cooling terminals are often used in buildings. It should be notable that the melting point is usually higher than the freezing point in the case of a composite PCM. Thus, the phase change temperature of PCM should be chosen rationally in order to correspond with the required chilled water temperature as well as to meet the thermal comfort. In addition, automatic control strategies should also be applied to keep the balance of the system.

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